

09763673.022601  
JC09 Rec'd PCT/PTO 26 FEB 2001 PCT\$

TRANSMITTAL LETTER TO THE UNITED STATES

ATTORNEY'S DOCKET NUMBER 49409

DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/763673

INTERNATIONAL APPLICATION NO.  
PCT/EP 99/07208

INTERNATIONAL FILING DATE  
29 September 1999

PRIORITY DATE CLAIMED  
1 October 1998

TITLE OF INVENTION: THERMOPLASTIC MOLDING COMPOSITIONS FOR INTERIOR APPLICATIONS IN MOTOR VEHICLES

APPLICANT(S) FOR DO/EO/US Michael FISCHER, Martin WEBER, Christophe GINSS, Stephan BERZ, Norbert KRESS

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
  2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
  3. /X/ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
  4. /X / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
  5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
    - a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
    - b./ / has been transmitted by the International Bureau.
    - c./ / is not required, as the application was filed in the United States Receiving Office (RO/USO).
  6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
  7. /X/ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
    - a./X/ are transmitted herewith (required only if not transmitted by the International Bureau).
    - b./ / have been transmitted by the International Bureau.
    - c./ / have not been made; however, the time limit for making such amendments has NOT expired.
    - d./ / have not been made and will not be made.
  8. /X/ A translation of the amendments to the claims under PCT Article 19(35 U.S.C. 371(c)(3)).
  9. / X/ An oath or declaration of the inventor(s)(35 U.S.C. 171(c)(4)).
  - 10./ / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
- 11./ / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  - 12./X / An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  - 13./X / A FIRST preliminary amendment.  
/ / A SECOND or SUBSEQUENT preliminary amendment.
  - 14./ / A substitute specification.
  - 15./ / A change of power of attorney and/or address letter.
  - 16.x / Other items or information.  
International Search Report  
International Preliminary Examination Report

09/763673

JC02 Rec'd PCT/PTO 26 FEB 2001

U.S. Appln. No. (If Known) INTERNATIONAL APPLN. NO.  
PCT/EP99/07208ATTORNEY'S DOCKET NO.  
49409

		CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted			
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the			
EPO or JPO.....	\$860.00	860.00	
International preliminary examination fee paid to USPTO			
(37 CFR 1.482).....	\$750.00		
No international preliminary examination fee paid to			
USPTO (37 CFR 1.482) but international search fee paid			
to USPTO (37 CFR 1.445(a)(2)).....\$700.00			
Neither international preliminary examination fee			
(37 CFR 1.482) nor international search fee			
(37 CFR 1.445(a)(2)) paid to USPTO .....\$ 970.00			
International preliminary examination fee paid to			
USPTO (37 CFR 1.482) and all claims satisfied pro			
-visions of PCT Article 33(2)-(4).....\$96.00			
<b>ENTER APPROPRIATE BASIC FEE AMOUNT = \$ 860.00</b>			
Surcharge of \$130.00 for furnishing the oath or declaration			
later than // 20 // 30 months from the earliest			
claimed priority date (37 CFR 1.492(e)).			
<u>Claims</u>	<u>Number Filed</u>	<u>Number Extra</u>	<u>Rate</u>
Total Claims	8 -20		X\$18.
Indep. Claims	1 -3		X\$80.
Multiple dependent claim(s) (if applicable)		+270.	
<b>TOTAL OF ABOVE CALCULATION</b>		<b>= 860.00</b>	
Reduction of 1/2 for filing by small entity, if applicable.			
Verified Small Entity statement must also be filed			
(Note 37 CFR 1.9, 1.27, 1.28).			
<b>SUBTOTAL</b>		<b>= 860.00</b>	
Processing fee of \$130. for furnishing the English			
translation later than // 20 // 30 months from the			
earliest claimed priority date (37 CFR 1.492(f)).			
<b>TOTAL NATIONAL FEE</b>		<b>= 860.00</b>	
Fee for recording the enclosed assignment (37 CFR 1.21(h)).			
The assignment must be accompanied by an appropriate cover			
sheet (37 CFR 3.28, 3.31) \$40.00 per property			
<b>TOTAL FEES ENCLOSED</b>		<b>= \$ 900.00</b>	
		Amount to be	
		refunded: \$	
		Charged \$	

a./X/ A check in the amount of \$ 900. to cover the above fees is enclosed.

b./ / Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.

c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.SEND ALL CORRESPONDENCE TO:  
KEIL & WEINKAUF  
1101 Connecticut Ave., N.W.  
Washington, D. C. 20036

SIGNATURE

Herbert B. Keil

NAME

Registration No. 18,967

## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of )  
FISCHER et al. ) BOX PCT  
)  
International Application )  
PCT/EP 99/07208 )  
)  
Filed: September 29, 1999 )  
)  
For: THERMOPLASTIC MOLDING COMPOSITIONS FOR INTERIOR  
APPLICATIONS IN MOTOR VEHICLES

PRELIMINARY AMENDMENT

Honorable Commissioner of  
Patents and Trademarks  
Washington, D.C. 20231

Sir:

Prior to examination, kindly amend the above-identified application as follows:

IN THE CLAIMS

Cancel claims 1-5 and insert new claims 6-13 on the attached sheets.

REMARKS

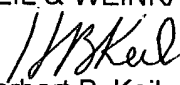
The claims were amended in the international preliminary examination under PCT Article 19 (35 USC 371(c)(3)). A translation of the amended claims is attached.

The claims have been amended further to eliminate multiple dependency and to put them in better form for U.S. filing. No new matter is included. A clean copy of the claims is attached.

Favorable action is solicited.

Respectfully submitted,

KEIL & WEINKAUF

  
Herbert B. Keil  
Reg. No. 18,967

1101 Connecticut Ave., N.W.  
Washington, D.C. 20036

(202)659-0100

## CLAIMS AS FILED IN 49409

--6. Moldings for motor vehicle interiors produced of a glass-fiber-reinforced thermoplastic molding composition comprising, based on the total of components A to D and, if desired, E and F, which in total give 100% by weight,

- a) as component A, from 10 to 97% by weight of at least one aromatic polyester,
- b) as component B, from 1 to 50% by weight of at least one particulate graft copolymer whose soft phase has a glass transition temperature below 0°C and whose median particle size is from 50 to 1000 nm,
- c) as component C, from 1 to 50% by weight of at least one copolymer made from the following monomers
  - c1) a component C1, from 50 to 90% by weight of at least one vinylaromatic monomer, and
  - c2) as component C2, from 10 to 25% by weight of acrylonitrile and/or methacrylonitrile,
- d) as component D, from 1 to 50% by weight of glass fibers,
- e) as component E, from 0 to 25% by weight of other compatible polymers homogeneously miscible with components A and/or C or dispersible in these, and
- f) as component F, from 0 to 10% by weight of conventional additives, such as UV stabilizers, oxidation retarders, lubricants and mold-release agents.

7. Moldings as claimed in claim 6, wherein component A is composed of

- a1) from 60 to 99% by weight of polybutylene terephthalate and
  - a2) from 1 to 40% by weight of polyethylene terephthalate.
8. Moldings as claimed in claim 6, wherein component B is composed of
- b1) from 50 to 90% by weight of a particulate graft base B1 made from the following monomers
    - b1.1) as component B11, from 75 to 99.9% by weight of a C<sub>1</sub>-C<sub>10</sub>-alkyl acrylate,
    - b1.2) as component B12, from 0.1 to 10% by weight of at least one polyfunctional monomer having at least two non-conjugated olefinic double bonds, and
    - b1.3) as component B13, from 0 to 24.9% by weight of one or more other copolymerizable monomers,
- and
- b2) from 10 to 50% by weight of a graft B2 made from the following monomers
    - b2.1) as component B21, from 50 to 90% by weight of a vinylaromatic monomer, and
    - b2.2) as component B22, from 10 to 50% by weight of acrylonitrile and/or methacrylonitrile.
9. Moldings as claimed in claim 6, wherein components B21 and/or C1 are unsubstituted styrene.
10. Moldings as claimed in claim 6, wherein component B1 is composed of components B11 and B12.
11. Moldings as claimed in claim 6, wherein component B is composed of from 10 to

90% by weight of a fine-particle graft copolymer whose median particle size is from 50 to 200 nm and from 10 to 90% by weight of a coarse-particle graft copolymer whose median particle size is from 250 to 1000 nm.

12. Moldings as claimed in claim 6 having one or more of the following features:
  - PV 3341 carbon emission < 40 µg of carbon/g 20
  - a grade better than 4 as the result of the DIN 50 011/PV 3900 odor test
  - Vicat B softening point > 145°C
  - ISO 179/1eU impact strength after 1000 h of continuous heat-aging at 130°C > kJ/m<sup>2</sup> and
  - DIN 53457 elongation at break after 1000 h of 30 continuous heat-aging at 130°C > 2%.
13. A method of use of molding compositions as defined in claim 6 for producing moldings for motor vehicle interiors, encompassing the step of thermoforming, extruding, injection molding, calendering, blow molding, compression molding, press sintering, or sintering of the molding compositions. --

**AS ORIGINALLY FILED**

NAE 19980620PC

IB/XS/gc

BASF Aktiengesellschaft

---

**Thermoplastic molding compositions for interior  
applications in motor vehicles**

---

The invention relates to glass-fiber-reinforced thermoplastic molding compositions, moldings made  
5 therefrom, and also to the use of the molding compositions to produce the moldings.

Moldings made from polymeric materials and used in the interior of motor vehicles have to meet high  
10 requirements for mechanical properties, surface properties, aging performance, and also odor performance. Various polymeric materials are currently used to produce moldings for interior applications in motor vehicles.

15 One material used is glass-fiber-reinforced ABS/PC (a polymer blend made from acrylonitrile-butadiene-styrene copolymer and polycarbonate). However, this material has unsatisfactory UV resistance, poor heat-aging  
20 performance (toughness and elongation at break after heat-aging), disadvantageous surface properties, and also in particular poor odor performance. For the purposes of the present invention, odor performance is the tendency of materials, after a specified duration  
25 of aging under particular temperature and climatic conditions, to give off volatile constituents which have a discernible odor.

Another material used is glass-fiber-reinforced impact-modified SMA (styrene-maleic anhydride copolymer). SMA,  
30 too, has unsatisfactory surface properties, poor heat-aging resistance, and also poor odor performance.

- 2 -

The materials mentioned above also have poor heat resistance, expressed in terms of a low Vicat B softening point (Vicat B < 130°C). Good heat resistance and heat-aging resistance of the materials used is, however, essential since the temperature of the motor vehicle interior can rise considerably, especially when exposed to solar radiation.

The disadvantages mentioned above can be removed by using polymeric materials based on PBT/ASA/PSAN (polymer blends made from polybutylene terephthalate, acrylonitrile-styrene-acrylate copolymer and polystyrene-acrylonitrile copolymer). Materials of this type are generally disclosed in DE-A 39 11 828. The working examples relate to molding compositions in which the PSAN copolymers have a high proportion of acrylonitrile. However, moldings made from these molding compositions also have poor emission performance.

It is an object of the present invention to provide molding compositions suitable for producing moldings which are used in the interior of motor vehicles and have an advantageous property profile in terms of their mechanical, optical and perceptual properties, and also in particular have good heat resistance and heat-aging resistance, and good emission performance and/or odor performance.

We have found that this object is achieved by means of a glass-fiber-reinforced thermoplastic molding composition comprising, based on the total of components A to D and, if desired, E and F, which in total give 100% by weight,

a) as component A, from 10 to 97% by weight of at least one aromatic polyester,



- 3 -

- 5       b) as component B, from 1 to 50% by weight of at least one particulate graft copolymer whose soft phase has a glass transition temperature below 0°C and whose median particle size is from 50 to 1000 nm,
- 10       c) as component C, from 1 to 50% by weight of at least one copolymer made from the following monomers
- 15           c1) as component C1, from 50 to 90% by weight of at least one vinylaromatic monomer, and
- c2) as component C2, from 10 to 25% by weight of acrylonitrile and/or methacrylonitrile,
- 20       d) as component D, from 1 to 50% by weight of glass fibers,
- 25       e) as component E, from 0 to 25% by weight of other compatible polymers homogeneously miscible with components A and/or C or dispersible in these, and
- f) as component F, from 0 to 10% by weight of conventional additives, such as UV stabilizers, carbon black, pigments, antioxidants, lubricants and mold-release agents.

30       The novel molding composition comprises, as component A, from 10 to 97% by weight, preferably from 20 to 75% by weight, particularly preferably from 30 to 60% by weight, of an aromatic polyester. The polyesters present in the novel molding compositions are known per se.

35       The polyesters may be prepared by reacting terephthalic acid, its esters or other ester-forming derivatives, with 1,4-butanediol, 1,3-propanediol or, respectively, 1,2-ethanediol, in a manner known per se.

- 4 -

Up to 20 mol% of the terephthalic acid may be replaced by other dicarboxylic acids. Those which may be mentioned, merely as examples, are naphthalenedi-  
5 carboxylic acids, isophthalic acid, adipic acid, azeleic acid, sebacic acid, dodecanedioic acid and cyclohexanedicarboxylic acids, mixtures of these carboxylic acids, and ester-forming derivatives of the same.

10

Up to 20 mol% of the dihydroxy compounds 1,4-butanediol, 1,3-propanediol or, respectively, 1,2-ethanediol may be replaced by other dihydroxy compounds, e.g. 1,6-hexanediol, 1,4-hexanediol, 1,4-  
15 cyclohexanediol, 1,4-di(hydroxymethyl)cyclohexane, bisphenol A, neopentyl glycol, mixtures of these diols, or also ester-forming derivatives of the same.

Preferred aromatic polyesters are polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT) and in particular polybutylene terephthalate (PBT), whose formation involves exclusively terephthalic acid and the appropriate diols 1,2-ethanediol, 1,3-propanediol and 1,4-butanediol. Some or  
20 all of the aromatic polyesters may be used in the form of recycled polyester materials, such as PET regrind from bottle material or from wastes from bottle production.

30 In a particularly preferred embodiment component A is composed of

- a1) from 60 to 99% by weight, in particular from 80 to 95% by weight, of polybutylene terephthalate, and  
35 a2) from 1 to 40% by weight, in particular from 5 to 20% by weight, of polyethylene terephthalate.

- 5 -

The novel molding composition comprises, as component B, from 1 to 50% by weight, preferably from 1 to 25% by weight, particularly preferably from 2 to 15% by weight, in particular from 2 to 10% by weight, of at least one particulate graft copolymer with a glass transition temperature of the soft phase below 0°C and with a median particle size of from 50 to 1000 nm.

Component B is preferably a graft copolymer made from

b1) from 50 to 90% by weight of a particulate graft base B1 with a glass transition temperature below 0°C, and

b2) from 10 to 50% by weight of a graft B2 made from the following monomers

b21) as component B21, from 50 to 90% by weight of a vinylaromatic monomer, and

b22) as component B22, from 10 to 49% by weight of acrylonitrile and/or methacrylonitrile.

The particulate graft base B1 may be composed of from 70 to 100% by weight of a conjugated diene and from 0 to 30% by weight of a bifunctional monomer having two non-conjugated olefinic double bonds. Graft bases of this type are used, for example, as component B in ABS polymers or MBS polymers.

In a preferred embodiment of the invention the graft base B1 is composed of the following monomers:

b11) as component B11, from 75 to 99.9% by weight of a C<sub>1</sub>-C<sub>10</sub>-alkyl acrylate,

b12) as component B12, from 0.1 to 10% by weight of at least one polyfunctional monomer having

- 6 -

at least two non-conjugated olefinic double bonds, and

5        b13) as component B13, from 0 to 24.9% by weight  
      of one or more other copolymerizable  
      monomers.

10       The graft base B1 is an elastomer whose glass  
      transition temperature is preferably below -20°C,  
      particularly preferably below -30°C.

15       The main monomers B11 used to prepare the elastomer are  
      acrylates having from 1 to 10 carbon atoms, in  
      particular from 4 to 8 carbon atoms, in the alcohol  
      component. Particularly preferred monomers B11 are  
      isobutyl and n-butyl acrylate, and also 2-ethylhexyl  
      acrylate, particularly preferably the latter two.

20       Besides the acrylates, the crosslinking monomer B12  
      used is from 0.1 to 10% by weight, preferably from 0.1  
      to 5% by weight, particularly preferably from 1 to 4%  
      by weight, of a polyfunctional monomer having at least  
      two non-conjugated olefinic double bonds. Examples of  
      these are divinylbenzene, diallyl fumarate, diallyl  
25       phthalate, triallyl cyanurate, triallyl isocyanurate,  
      tricyclodeceny acrylate and dihydrodicyclopentadienyl  
      acrylate, particularly preferably the latter two.

30       Besides the monomers B11 and B12, the structure of the  
      graft base B1 may also involve up to 24.9% by weight,  
      preferably up to 20% by weight, of other  
      copolymerizable monomers, preferably 1,3-butadiene,  
      styrene,  $\alpha$ -methylstyrene, acrylonitrile,  
      methacrylonitrile and C<sub>1</sub>-C<sub>8</sub>-alkyl methacrylates, or  
35       mixtures of these monomers. In a particularly preferred  
      embodiment no 1,3-butadiene is present in the graft  
      base B1, and the graft base B1 in particular is  
      composed exclusively of components B11 and B12.

- 7 -

Grafted onto the graft base B1 there is a graft B2 made from the following monomers:

5           b21) as component B21, from 50 to 90% by weight, preferably from 60 to 90% by weight, particularly preferably from 65 to 80% by weight, of a vinylaromatic monomer, and

10           b22) as component B22, from 10 to 50% by weight, preferably from 10 to 40% by weight, particularly preferably from 20 to 35% by weight, of acrylonitrile or methacrylonitrile or mixtures of these.

15   Examples of vinylaromatic monomers are unsubstituted styrene and substituted styrenes, such as  $\alpha$ -methylstyrene, p-chlorostyrene and p-chloro- $\alpha$ -methylstyrene. Preference is given to unsubstituted styrene and  $\alpha$ -methylstyrene, particularly unsubstituted  
20   styrene.

In one embodiment of the invention the median particle size of component B is from 50 to 200 nm, preferably about 100 nm.

25   In another embodiment of the invention the median particle size of component B is from 200 to 1000 nm, preferably about 500 nm.

30   In a particularly preferred embodiment of the invention component B has bimodal particle size distribution and is composed of from 10 to 90% by weight, preferably from 30 to 90% by weight, particularly preferably from 50 to 75% by weight, of a fine-particle graft copolymer  
35   with a median particle size of from 50 to 200 nm, preferably about 100 nm, and from 10 to 90% by weight, preferably from 10 to 70% by weight, particularly preferably from 25 to 50% by weight, of a coarse-

- 8 -

particle graft copolymer with a median particle size of from 250 to 1000 nm, preferably about 500 nm.

The median particle size and particle size distribution given are the sizes determined from the integral mass distribution. The median particle sizes according to the invention are in all cases the ponderal median of the particle sizes. The determination of these is based on the method of W. Scholtan and H. Lange, Kolloid-Z. und Z.-Polymere 250 (1972), pages 782-796, using an analytical ultracentrifuge. The ultracentrifuge measurement gives the integral mass distribution of the particle diameters in a specimen. From this it is possible to deduce what percentage by weight of the particles has a diameter identical to or smaller than a particular size. The median particle diameter, which is also termed the  $d_{50}$  of the integral mass distribution, is defined here as the particle diameter at which 50% by weight of the particles have a diameter smaller than that corresponding to the  $d_{50}$ . Equally, 50% by weight of the particles then have a larger diameter than the  $d_{50}$ . To describe the breadth of the particle size distribution of the rubber particles,  $d_{10}$  and  $d_{90}$  values given by the integral mass distribution are utilized alongside the  $d_{50}$  value (median particle diameter). The  $d_{10}$  and  $d_{90}$  of the integral mass distribution are defined similarly to the  $d_{50}$  with the difference that they are based on, respectively, 10 and 90% by weight of the particles. The quotient

30

$$\frac{d_{90} - d_{10}}{d_{50}} = Q$$

is a measure of the breadth of the particle size distribution. Emulsion polymers A which can be used according to the invention as component A preferably have  $Q$  less than 0.5, in particular less than 0.35.

35

- 9 -

The graft copolymer B generally has one or more stages, i.e. it is a polymer composed of a core and of one or more shells. The polymer is composed of a base (graft core) B1 and of, grafted onto this, one, or preferably  
5 more than one, stages B2 (graft), known as grafts or graft shells.

By grafting one or more times it is possible to apply one or more graft shells to the rubber particles. Each  
10 graft shell may have a different make up. In addition to the grafting monomers and together with these, polyfunctional crosslinking monomers or monomers containing reactive groups may be grafted on (see, for example, EP-A 0 230 282, DE-A 36 01 419,  
15 EP-A 0 269 861).

In one embodiment of the invention crosslinked acrylate polymers with a glass transition temperature below 0°C serve as graft base B1. The crosslinked acrylate  
20 polymers should preferably have a glass transition temperature below -20°C, in particular below -30°C.

In principle the structure of the graft copolymer may also have two or more layers, where at least one inner  
25 layer has a glass transition temperature below 0°C and the outermost layer should have a glass transition temperature above 23°C.

In a preferred embodiment the graft B2 is composed of  
30 at least one graft shell. The outermost graft shell of these has a glass transition temperature above 30°C. A polymer formed from the monomers of the graft B2 would have a glass transition temperature above 80°C.

35 Suitable preparation processes for graft copolymers B are emulsion, solution, bulk and suspension polymerization. The graft copolymers B are preferably prepared by free-radical emulsion polymerization, at temperatures of from 20 to 90°C using water-soluble

- 10 -

and/or oil-soluble initiators, such as peroxodisulfate or benzoyl peroxide, or with the aid of redox initiators. Redox initiators are also suitable for polymerization below 20°C.

5

Suitable emulsion polymerization processes are described in DE-A-28 26 925, DE-A 31 49 358 and in DE-C-12 60 135.

10 The graft shells are preferably built up in the emulsion polymerization process as described in DE-A-32 27 555, 31 49 357, 31 49 358 and 34 14 188. The specified setting of the particle sizes according to the invention at from 50 to 1000 nm preferably takes  
15 place by the methods described in DE-C-12 60 135 and DE-A-28 26 925, or in Applied Polymer Science, Vol. 9 (1965), page 2929. The use of polymers with different particle sizes is known, for example, from DE-A-28 26 925 and US 5,196,480.

20

The novel molding compositions comprise, as component C, from 1 to 50% by weight, preferably from 10 to 25% by weight, particularly preferably from 12 to 20% by weight, of a copolymer made from the following  
25 monomers:

c1) as component C1, from 75 to 90% by weight, preferably from 77 to 90% by weight, particularly preferably from 81 to 90% by weight, of at least  
30 one vinylaromatic monomer, and

c2) as component C2, from 10 to 25% by weight, preferably from 10 to 23% by weight, particularly preferably from 10 to 19% by weight, in particular  
35 from 15 to 19% by weight, of acrylonitrile and/or methacrylonitrile.

Suitable vinylaromatic monomers are the abovementioned monomers C1 and the vinylaromatic monomers mentioned



- 11 -

above as component B21. Component C is preferably an amorphous polymer as described above for graft B2. In one embodiment of the invention component C comprises a copolymer of styrene and/or  $\alpha$ -methylstyrene with acrylonitrile. The acrylonitrile content in these copolymers of component C here is not above 25% by weight and is generally from 10 to 25% by weight, preferably from 10 to 22% by weight, particularly preferably from 10 to 19% by weight, in particular from 15 to 19% by weight. Component C also includes the free, ungrafted styrene-acrylonitrile copolymers produced during the graft copolymerization to prepare component B. Depending on the conditions selected in the graft copolymerization for preparing the graft copolymer B, it is possible that a sufficient proportion of component C may already have been formed during the graft copolymerization. However, it will generally be necessary for the products obtained during the graft copolymerization to be blended with additional and separately prepared component C.

This additional and separately prepared component C may preferably be a styrene-acrylonitrile copolymer, an  $\alpha$ -methylstyrene-acrylonitrile copolymer or an  $\alpha$ -methylstyrene-styrene-acrylonitrile terpolymer. It is important that the acrylonitrile content in the copolymers C does not exceed 25% by weight, in particular 19% by weight. The copolymers may be used for component C either individually or as a mixture, and the additional and separately prepared component C of the novel molding compositions may, for example, therefore be a mixture of a styrene-acrylonitrile copolymer (PSAN) and an  $\alpha$ -methylstyrene-acrylonitrile copolymer. The acrylonitrile content of the different copolymers of component C may also vary. However, component C is preferably composed simply of one or more styrene-acrylonitrile copolymers, which may have differing acrylonitrile content. In a particularly

- 12 -

preferred embodiment component C is composed simply of one styrene-acrylonitrile copolymer.

The novel molding compositions comprise, as component  
5 D, from 1 to 50% by weight, preferably from 5 to 50% by weight, particularly preferably from 7 to 45% by weight, in particular from 10 to 40% by weight, of glass fibers. These are commercially available products.

10

In the molding composition these preferably have an average length of from 0.1 to 0.5 mm, preferably from 0.1 to 0.4 mm, and a diameter of from 6 to 20  $\mu\text{m}$ . Particular preference is given to E-glass fibers. To  
15 achieve better adhesion the glass fibers may have been coated with organosilanes, epoxysilanes or other polymer coatings.

The novel molding compositions may comprise, as  
20 component E, from 0 to 25% by weight of other polymers homogeneously miscible with components A and/or C or dispersible in these. Examples of those which may be used are appropriate conventional (grafted) rubbers, such as ethylene-vinyl acetate rubbers, silicone  
25 rubbers, polyether rubbers, hydrogenated diene rubbers, polyalkenamer rubbers, acrylate rubbers, ethylene-propylene rubbers, ethylene-propylene-diene rubbers and butyl rubbers, methyl methacrylate-butadiene-styrene (MBS) rubbers, methyl methacrylate-butyl acrylate-  
30 styrene rubbers, as long as these are miscible with the mixed phase formed from components A, B and C or are dispersible within this. Preference is given to acrylate rubber, ethylene-propylene (EP) rubber and ethylene-propylene-diene (EPDM) rubber. It is also  
35 possible to use polymers or copolymers miscible or compatible with the mixed phase formed from components B and C, for example polycarbonates, polymethacrylates, in particular PMMA, polyphenylene ethers or syndiotactic polystyrene. It is also possible to use

- 13 -

reactive rubbers which link to the polyester (component A) via a covalent bond, for example particulate acrylate rubbers and/or polyolefin rubbers grafted with anhydrides, such as maleic anhydride, or with epoxy compounds, such as glycidyl methacrylate. Finally, it is also possible to use one or more polymers or copolymers which are present at the boundary between the amorphous phase formed from components B and/or C and the crystalline or semicrystalline phase formed from component A, and thus improve the adhesion between the two phases. Examples of polymers of this type are graft copolymers made from PBT and PSAN and segmented copolymers, such as block copolymers or multiblock copolymers made from at least one segment of PBT with  $M_w > 1000$  and at least one segment of PSAN or a segment compatible/miscible with PSAN with  $M_w > 1000$ .

The novel molding compositions comprise, as component F, from 0 to 10% by weight of conventional additives. Examples of additives of this type are: UV stabilizers, oxidation retarders, lubricants, mold-release agents, dyes, pigments, colorants, nucleating agents, antistats, antioxidants, stabilizers to improve thermal stability, to increase light stability, to raise hydrolysis resistance and chemicals resistance, agents to prevent decomposition by heat, and in particular the lubricants useful for producing moldings. These other additives may be metered in at any stage of the preparation process, but preferably at an early juncture so as to make use at an early stage of the stabilizing effects (or other specific effects) of the additive. Heat stabilizers or oxidation retarders are usually metal halides (chlorides, bromides or iodides) derived from metals in group I of the Periodic Table of the Elements (for example Li, Na, K or Cu).

Suitable stabilizers are the usual hindered phenols, or else vitamin E or compounds of similar structure. HALS stabilizers (hindered amine light stabilizers) are also

- 14 -

suitable, as are benzophenones, resorcinols, salicylates, benzotriazoles and other compounds (for example Irganox®, Tinuvin®, such as Tinuvin® 770 (HALS absorbers, bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate) or Tinuvin® P (UV absorber - (2H-benzotriazol-2-yl)-4-methylphenol) or Topanol®). The amounts of these usually used are up to 2% by weight, based on the entire mixture.

10 Examples of suitable lubricants and mold-release agents are stearic acids, stearyl alcohol, stearates and in general higher fatty acids, derivatives of these and appropriate fatty acid mixtures having from 12 to 30 carbon atoms. The amounts of these additives are from 15 0.05 to 1% by weight.

Other possible additives are silicone oils, oligomeric isobutylene, or similar substances. The usual amounts are from 0.05 to 5% by weight. It is also possible to 20 use pigments, dyes, color brighteners, such as ultramarine blue, phthalocyanines, titanium dioxide, cadmium sulfides and derivatives of perylenetetra-carboxylic acid. Another additive which may be used is carbon black, either pure or as a masterbatch.

25 The amounts used of processing aids and stabilizers, such as UV stabilizers, lubricants and antistats, are usually from 0.01 to 5% by weight, based on the entire molding composition.

30 It is also possible to use amounts of, for example, up to 5% by weight, based on the entire molding composition, of nucleating agents, such as talc, calcium fluoride, sodium phenylphosphinate, alumina or 35 finely divided polytetrafluoroethylene. Amounts of up to about 5% by weight, based on the molding composition, of plasticizers, such as dioctyl phthalate, dibenzyl phthalate, butyl benzyl phthalate, hydrocarbon oils, N-(n-butyl)benzenesulfonamide, or o-

- 15 -

or p-tolueneethylsulfonamide are advantageously added. It is also possible to add amounts of up to about 5% by weight, based on the molding composition, of colorants, such as dyes and pigments.

5

Components A, B, C, D and, if desired, E and F may be mixed in any desired manner using any of the known methods. Components A - D and, if desired, E and F may be mixed as such, or else in the form of mixtures of one component with one or more of the other components. For example, component B may be premixed with some or all of component C and, if desired, with components E and F, and then mixed with the other components. If components B and C have been prepared, for example, by emulsion polymerization, the resultant polymer dispersions may be mixed with one another, followed by joint precipitation of the polymers and work-up of the polymer mixture. However, it is preferable to blend components B and C by joint extrusion, kneading or rolling of the components, and if necessary components B and C may have been isolated previously from the solution or aqueous dispersion obtained during the polymerization. The novel thermoplastic molding compositions may, for example, be prepared by melting component A in an extruder with each of the components B and C or with a mixture made from these and, if desired, with components E and F, and feeding the glass fibers via an inlet to the extruder.

30 The novel molding compositions may be processed by known methods of thermoplastic processing to give moldings. In particular, these may be produced by thermoforming, extruding, injection molding, calendering, blow molding, compression molding, press sintering, thermoforming or sintering, preferably by injection molding. The moldings which can be produced from the novel molding compositions are also provided by the present invention.

35

- 16 -

The moldings produced from the novel molding compositions have only low emissions of volatile constituents with a discernible odor. The odor performance of polymer materials is assessed to  
5 DIN 50011/PV 3900 and this applies to components in motor vehicle interiors. For the novel moldings the result of odor testing to this standard is generally better than grade 5, preferably better than grade 4, particularly preferably better than grade 3.5. The  
10 carbon emission of the moldings to PV 3341 is generally  $< 50 \mu\text{g/g}$ , preferably  $< 40 \mu\text{g/g}$ , particularly preferably  $< 30 \mu\text{g/g}$ .

The novel moldings also have good heat resistance. The  
15 Vicat B softening point is generally  $> 130^\circ\text{C}$ , preferably  $> 140^\circ\text{C}$ , particularly preferably  $> 150^\circ\text{C}$ .

The novel moldings also have good heat-aging performance. For example, the impact strength of the  
20 novel moldings to ISO 179/1eU after 1000 hours of continuous heat-aging at  $130^\circ\text{C}$  is generally  $> 25 \text{ kJ per m}^2$ , preferably  $> 30 \text{ kJ per m}^2$ . The elongation at break of the novel moldings after 1000 hours of continuous heat-aging at  $130^\circ\text{C}$  is generally  $> 1.5\%$ , preferably  $>$   
25  $2\%$ .

The novel moldings also have good mechanical properties. For example, their modulus of elasticity is generally  $> 6000 \text{ MPa}$ , preferably  $> 6500 \text{ MPa}$ , their  
30 yield stress is generally  $> 100 \text{ MPa}$ , preferably  $> 110 \text{ MPa}$ , their ISO 179/1eU impact strength is generally  $> 40 \text{ kJ per m}^2$ , preferably  $> 45 \text{ kJ per m}^2$ , their impact strength without prior heat-aging to ISO 179/1eA is generally  $> 6 \text{ kJ per m}^2$  and their HDT B  
35 (measured to ISO 75 method B) is generally  $> 190^\circ\text{C}$ , preferably  $> 200^\circ\text{C}$ , and their flowability (MVR  $250^\circ\text{C}$ /under  $10 \text{ kp}$  load) is  $> 20 \text{ g/cm}^3$ , preferably  $> 40 \text{ g/cm}^3$ .

- 17 -

Even after 1000 h of continuous heat-aging at 130°C, the novel moldings do not show brittle failure in the penetration test at -30°C (2 and 3 mm sheet thickness, to ISO 6603/2).

5

The high heat resistance, good heat-aging resistance, good mechanical properties and good surface properties of the novel moldings make them suitable for a wide variety of applications. The following are mentioned  
10 merely as examples: camera casings, tube sections for binoculars, vapor ducts for vapor-extraction hoods, parts for pressure cookers, housings for hot-air grills and pump housings.

15 The abovementioned properties make the novel moldings particularly suitable for applications in motor vehicles.

Examples of novel moldings produced in particular from  
20 the novel molding compositions are parts such as light-switch housings, lamp housings, housings for the central electrical system, multipoint connectors, plug connectors, housings for ABS controls, and supports for identification plates and also roof racks.

25

The good emission performance of the novel moldings makes them particularly suitable for applications in motor vehicle interiors. The novel moldings produced from the novel molding compositions are therefore in  
30 particular protective coverings, stowage compartments, dashboard supports, door breasts, parts for the center console, and also retaining elements for radio and air-conditioning system, covers for the center console, covers for radio, air-conditioning system and ashtray,  
35 prolongations of the center console, stowage pockets, storage areas for the driver's door and front passenger's door, storage areas for the center console, components for the driver's and passenger's seats, such as seat coverings, defroster ducts, internal mirror

- 18 -

housings, sun-roof elements, such as sun-roof frames, protective surrounds for instruments, instrument sockets, upper and lower shells for the steering column, air-conveying ducts, air blowers and adapters  
5 for personal airflow devices and defroster ducts, door side coverings, coverings in the knee area, air-outlet nozzles, defroster apertures, switches and levers. These applications are just some examples of possible applications in motor vehicle interiors.

10

The invention also provides the use of the novel molding compositions for producing the moldings mentioned.

15 The examples below describe the invention in greater detail:

**Examples:**

20 Examples 1 to 4 and comparative example

The amounts of polybutylene terephthalate (PBT), standard or recycled polyethylene terephthalate (PET), glass fibers, graft rubbers P1 and P2, copolymers PSAN  
25 1, PSAN 2 and PSAN 3, and additives given in Table 1 were mixed in a screw-extruder at from 250 to 270°C. The test specimens corresponding to the relevant DIN standards were injection-molded from the resultant molding compositions.

30

P1 is a fine-particle ASA graft rubber with 25% by weight of acrylonitrile in the SAN graft shell with an average particle size of about 100 nm.

35 P2 is a coarse-particle ASA graft rubber with an average particle diameter of about 500 nm.

PSAN 1 is a styrene-acrylonitrile copolymer with 25% by weight of acrylonitrile.



- 19 -

PSAN 2 is a styrene-acrylonitrile copolymer with 19% by weight of acrylonitrile.

- 5 PSAN 3 is a styrene-acrylonitrile copolymer with 35% by weight of acrylonitrile.

Emission performance was assessed to PV 3341, and also to DIN 50011/PV 3900 C3.

- 10 Odor emission to DIN 50011/PV 3900 C3 was measured as follows:

- 50 cm<sup>3</sup> of specimen material was tightly sealed in a 1 l vessel with odorless gasket and lid, and this was  
15 stored for 2 hours in a preheated heating chamber with air circulation at 80°C. The test vessel was removed from the heating chamber and then cooled to 60°C before assessment by at least 3 testers. Odor was assessed using the assessment scale with grades 1 to 6, and  
20 intermediate half grades are permissible.

Assessment scale:

- Grade 1 Not detectable  
25 Grade 2 Detectable but not unpleasant  
Grade 3 Clearly detectable but still not unpleasant  
Grade 4 Unpleasant  
Grade 5 Very unpleasant  
Grade 6 Intolerable

30

Table 2 gives the results of the odor test and the results of the mechanical tests also carried out.

Table 1:

Starting material [% by weight]	Comparative example	Example 1	Example 2	Example 3
PBT	46.62	46.62	46.62	46.62
Glass fiber	20	20	20	20
PET	9	9	9	
P 1	12	3	3	
P 2		2	2	12
PSAN 1		17		
PSAN 2			16	10
PSAN 3	10			
Loxiol	0.58	0.58	0.58	0.58
Carbon black	1.8	1.8	1.8	1.8

Table 2:

	Comparative example	Example 1	Example 2	Example 3
Flowability measured by MVR 250/10 [cm <sup>3</sup> /10 min]	18	16	58	25
Density [g/cm <sup>3</sup> ]	1.391	1.388	1.367	1.372
Impact strength to ISO 179/1eU	49	48	52	53
Notched impact strength to ISO 179/1eA [kJ/m <sup>2</sup> ]	6.7	7.0	7.2	7.6
Modulus of elasticity to DIN 53457 [MPa]	6850	7600	7600	6800
Breaking stress to DIN 53457 [MPa]	103	118	120	103
Elongation at break to DIN 53457 [%]	2.4	2.3	2.5	2.4
Penetration energy to ISO 6603/2 [Nm]	2.5	2	3	3
HDT to ISO 75 B [°C]	208	207	205	203
Odor test to PV 3900 C3 [Grade]	4	3.5	3	3.5
Carbon emission to PV 3341 [µg C/g]	70	38	28	38

As enclosed to IPER

## We claim:

1. The use of glass-fiber-reinforced thermoplastic molding composition comprising, based on the total of components A to D and, if desired, E and F, which in total give 100% by weight,
  - a) as component A, from 10 to 97% by weight of at least one aromatic polyester,
  - b) as component B, from 1 to 50% by weight of at least one particulate graft copolymer whose soft phase has a glass transition temperature below 0°C and whose median particle size is from 50 to 1000 nm,
  - c) as component C, from 1 to 50% by weight of at least one copolymer made from the following monomers
    - c1) a component C1, from 50 to 90% by weight of at least one vinylaromatic monomer, and
    - c2) as component C2, from 10 to 25% by weight of acrylonitrile and/or methacrylonitrile,
  - d) as component D, from 1 to 50% by weight of glass fibers,
  - e) as component E, from 0 to 25% by weight of other compatible polymers homogeneously miscible with components A and/or C or dispersible in these, and
  - f) as component F, from 0 to 10% by weight of conventional additives, such as UV stabilizers, oxidation retarders, lubricants and mold-release agentsfor producing moldings for motor vehicle interiors.
2. The use as claimed in claim 1, wherein component A is composed of

a1) from 60 to 99% by weight of polybutylene terephthalate and

a2) from 1 to 40% by weight of polyethylene terephthalate.

3. The use as claimed in claim 1 or 2, wherein component B is composed of

b1) from 50 to 90% by weight of a particulate graft base B1 made from the following monomers

b1.1) as component B11, from 75 to 99.9% by weight of a C<sub>1</sub>-C<sub>10</sub>-alkyl acrylate,

b1.2) as component B12, from 0.1 to 10% by weight of at least one polyfunctional monomer having at least two non-conjugated olefinic double bonds, and

b1.3) as component B13, from 0 to 24.9% by weight of one or more other copolymerizable monomers,  
and

b2) from 10 to 50% by weight of a graft B2 made from the following monomers

b2.1) as component B21, from 50 to 90% by weight of a vinylaromatic monomer, and

b2.2) as component B22, from 10 to 50% by weight of acrylonitrile and/or methacrylonitrile.

4. The use as claimed in any one of claims 1 to 3, wherein components B21 and/or C1 are unsubstituted styrene.

5. The use as claimed in any one of claims 1 to 4, wherein component B1 is composed of components B11 and B12.

### Abstract

A glass-fiber-reinforced thermoplastic molding composition comprises, based on the total of components A to D and, if desired, E and F, which in total give 100% by weight,

- a) as component A, from 10 to 97% by weight of at least one aromatic polyester,
- b) as component B, from 1 to 50% by weight of at least one particulate graft copolymer whose soft phase has a glass transition temperature below 0°C and whose median particle size is from 50 to 1000 nm,
- c) as component C, from 1 to 50% by weight of at least one copolymer made from the following monomers
  - c1) as component C1, from 50 to 90% by weight of at least one vinylaromatic monomer, and
  - c2) as component C2, from 10 to 25% by weight of acrylonitrile and/or methacrylonitrile,
- d) as component D, from 1 to 50% by weight of glass fibers,
- e) as component E, from 0 to 25% by weight of other compatible polymers homogeneously miscible with components A and/or C or dispersible in these, and
- f) as component F, from 0 to 10% by weight of conventional additives, such as UV stabilizers, oxidation retarders, lubricants and mold-release agents.

Moldings made from these molding compositions and used in motor vehicle interiors are also described, as is the use of the molding compositions to produce the moldings.

# Declaration, Power of Attorney

Page 1 of 4

0050/049409

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Thermoplastic molding compositions for interior applications in motor vehicles

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP99/07208

on September 29, 1999

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19845317.5	Germany	01 October 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

pctwpct001 - 25



**Declaration**

Page 2 of 4

0050/049409

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

_____	_____
(Application Number)	(Filing Date)
_____	_____
(Application Number)	(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

<b>Application Serial No.</b>	<b>Filing Date</b>	<b>Status (pending, patented, abandoned)</b>
-------------------------------	--------------------	--

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint **Messrs. HERBERT B. KEIL**, Registration Number 18,967; and **RUSSEL E. WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith. (2)

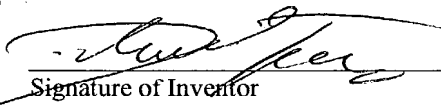
We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

## Declaration

Page 3 of 4

0050/049409

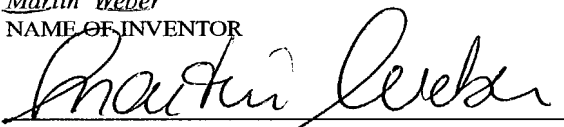
1-00  
Michael Fischer  
 NAME OF INVENTOR

  
 Signature of Inventor

Date 1/02/01

*Pater-Baroffio-Weg 29*  
 67071 Ludwigshafen  
 Germany DEX  
 Citizen of: Germany  
 Post Office Address: same as residence

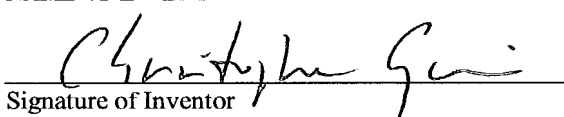
2-00  
Martin Weber  
 NAME OF INVENTOR

  
 Signature of Inventor

Date 1/02/01

*Diedesfelder Str. 26*  
 67487 Maikammer  
 Germany DEX  
 Citizen of: Germany  
 Post Office Address: same as residence

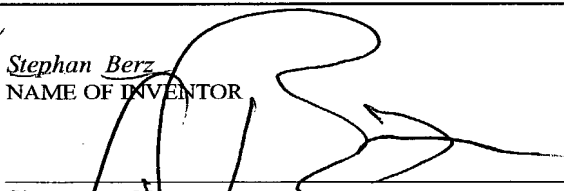
3-00  
Christophe Ginss  
 NAME OF INVENTOR

  
 Signature of Inventor

Date 1/02/01

*13, rue principale*  
 67120 Wolxheim  
 France FRF  
 Citizen of: France  
 Post Office Address: same as residence

4-00  
Stephan Berz  
 NAME OF INVENTOR

  
 Signature of Inventor

Date 1/02/01

*Schwarzbachstr.7b*  
 60529 Frankfurt  
 Germany DEX  
 Citizen of: Germany  
 Post Office Address: same as residence

09763673 022601

**Declaration**

Page 4 of 4

0050/049409

5-0 ✓  
Norbert Kreß  
NAME OF INVENTOR

Norbert Kreß  
Signature of Inventor

Date 1/02/01

Weinbrennerstr.8  
67069 Ludwigshafen-  
Germany DEU  
Citizen of: Germany  
Post Office Address: same as residence